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Viscoelastic Properties of (Cellulose Oligo-Oxymethylene Ether) Acylates II

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Abstract—The viscoelastic properties for a series of (cellulose oligo-oxymethylene ether) acylates, COA, were investigated, varying their side chain length in both the oxymethylene group and acyl group portions. It was found that for COA with acyl chain with length short as the acetate group, the change in the length of the oxymethylene chain caused remarkable difference in their viscoelastic properties, while for COA with such long acyl chain as the decanoate group it induced little difference. Furthermore, the difference in viscoelastic properties between COA and the corresponding cellulose acylate also became negligibly small when their acyl chain was long enough as the decanoate group. In the process of these consideration, the β and γ processes for COA were respectively assigned to be due to the micro-Brownian motion along the side chain, and the motion of the oxymethylene groups in the side chain.

Introduction

(Cellulose oligo-oxymethylene ether) acylates, hereinafter termed as COA, are different in chemical structure from the traditional series of cellulose acylates in that the oligo-oxymethylene groups intervene in between glucopyranose ring and the acyl side group¹⁾. The length of the oligo-oxymethylene chain or the number of the oxymethylene unit introduced in respective COA can be easily controlled through selecting dissolution condition of cellulose in paraformaldehyde/DMSO solvent system²⁾.

In our previous work³⁾, the viscoelastic properties of COA from acetate to valerate were studied by using dynamic mechanical measurements, from which three processes for all COA's and an additional process for the butylate and valerate were observed in the frequency and temperature ranges examined. These processes were labelled α , β , γ , and δ in order of decreasing temperature at which they were detected. These α to δ processes were respectively attributed to: micro-Brownian motion (α), motion of acyl side chain (β), local mode motion involving oxymethylene group

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(γ), and motion initiated by three or more methylene groups (δ). Among these processes, the dominant α and β processes were shown to be largely affected by the kind of COA, namely, the chain length of the linear acyl group introduced in the side chain. This indicates that the governing factor of the viscoelastic properties of COA is its side chain length. However, the side chain of COA is composed not only of acyl chain portion but also of oligo-oxymethylene chain portion. Therefore, it is important to clarify the effect of the length of oligo-oxymethylene chain on the viscoelastic properties of COA.

The present article describes dynamic mechanical properties of polymers in a series of COA from acetate to decanoate in relation to the chain length of the oxymethylene portion as well as that of the acyl portion in the side chain. All the samples employed here are almost amorphous in nature.

Experimental

Preparation of (cellulose oligo-oxymethylene ether) acylates

The method for preparing (cellulose oligo-oxymethylene ether) acylates used in this study is similar to that reported in our previous article³⁾. Dried cellulose powder (6 g) and paraformaldehyde (12 g) were well dispersed in dimethylsulfoxide (150 ml) at room temperature. The mixture was then kept at the specified dissolution condition (time and temperature) of cellulose in a 300 ml Erlenmeyer flask equipped with a condenser, to control the number of oxymethylene unit introduced in the side chain prior to introducing acyl groups. The cellulose solution so obtained was cooled to room temperature. Triethylamine (6 mol/glucose unit of cellulose) and one of a series of aliphatic anhydrides from acetic anhydride to decanoic anhydride (6 mol/glucose unit of cellulose) were added to the cooled cellulose solution with continuous stirring. After the reaction mixture was allowed to stand at room temperature for 5 hrs, it was poured into suitable precipitants to obtain the sample. The samples were completely peracylated.

Measurement of dynamic mechanical properties

Dynamic mechanical properties for filmed specimens were measured with a direct reading viscoelastometer (Toyo Baldwin Co., Ltd., Rheovibron DDV-II-C). Complex modulus and loss tangent were measured in the temperature range from -190°C to 200°C at a frequency of 110 Hz. The programmed heating rate was about $1^{\circ}\text{C}/\text{min}$. The size of specimen was 0.2 mm thick \times 2 mm wide \times 4 cm long for measurements in the temperature range from -190°C to 30°C and 1 mm thick \times 2 mm wide \times 2 cm long in the range from 30°C to 200°C .

Static tensile test

Static tensile tests for film specimens ($40 \times 2 \times 0.2$ mm) were carried out in a conditioned room (20°C, 65% RH) using an instron type testing instrument (Shinkoh Communication Industry Co., TOM-5000X). Elongation was applied to the specimen with a constant of 10 mm/min.

Results and discussion

The acetyl contents (AC%) of cellulose acetate with DS value of 3.0 is known to be 62.5%. However, the AC% of (Cellulose oligo-oxymethylene ether) acetate, CAcOM, with DS of 3.0 differs substantially from that of cellulose acetate, being ca. 20% lower. The reason for a considerable lowering of AC% can be ascribed to the introduction of oligo-oxymethylene groups-(CH₂O)_s-in between glucopyranose ring and acyl group in the side chain. Based on this difference in AC% between cellulose acetate and CAcOM whose DS values are both estimated to be 3.0, the number of oxymethylene units introduced in the side chain can be calculated. Table 1 shows the relationship between dissolution condition (time and temperature) of cellulose and *s* determined from CAcOM. It can be seen that the values of *s*, which indicate the measure of the oxymethylene chain length increase from 1.2 to 2.2 in order of dissolution condition A, B, C, and D.

Table 1.

Dissolution condition of cellulose			
Temperature (°C)	Time (min)	<i>s</i> in -(CH ₂ O) _s -	Symbol
120	180	1.2	A
120	80	1.8	B
120	25	2.0	C
110	35	2.2	D

The conditions B and C were adopted only for (cellulose oligo-oxymethylene ether) acetate

In the previous work³⁾, we studied the tensile properties of COA from acetate to valerate, and found that by increasing the number of carbons, *n*, in the acyl side chain, mechanical properties of COA shifted from a strong and tough type to an elastomeric one. On the other hand, since each side chain of COA consists of both the acyl and oxymethylene portions, i.e. -(CH₂O)_s-COR, the tensile properties of COA may also be affected when the side chain varies at the oxymethylene portion instead of acyl portion. Figure 1 shows the stress-strain diagrams of CAcOM(A, B, C, and D) in tension measured at 20°C and 65%R.H. Symbols used in parenthesis

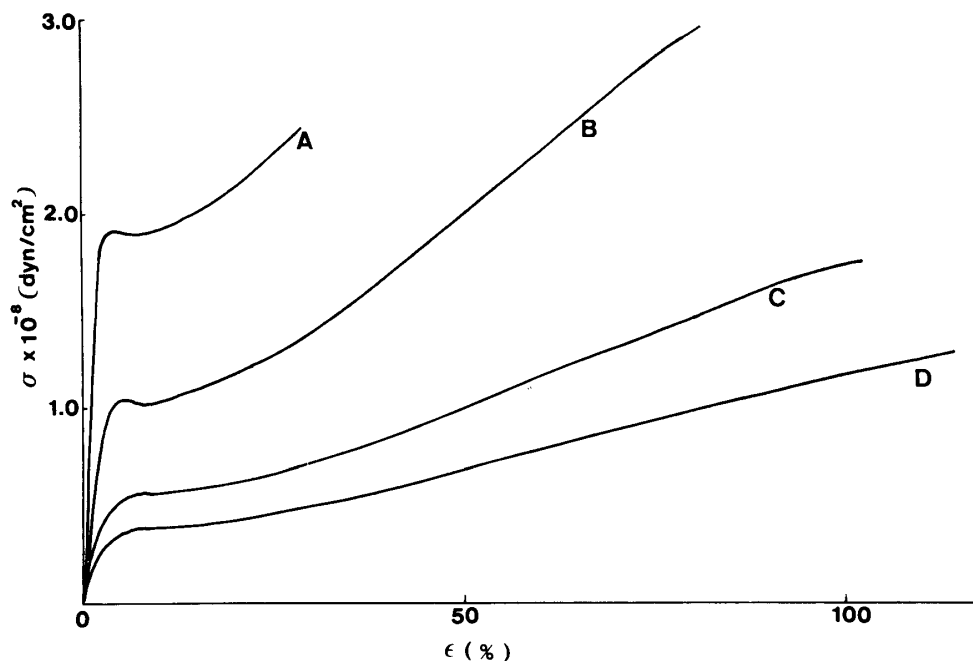


Fig. 1. Stress-strain diagrams of CAcOM (A, B, C, and D).

hereinafter indicate dissolution condition mentioned above. These diagrams are similar in shape, and have a yield point. However, as s in the oxymethylene part increases, the Young's modulus E and a yield strength σ_y decrease while maximum elongation ϵ_y increases. This trend corresponds to that observed for COA when n increased from 2 to 5 in the acyl group portion³⁾. From these results, it is known that changing length of the oxymethylene or acyl chains gives similar effect to the tensile properties of COA despite their difference in molecular structure. In this connection, it can be noted that the stress-strain diagrams were obtained in the temperature region of the β process for CAcOM. Thus, there exists a close relation between the molecular motion in the β process and the stress-strain curves examined. Therefore, the results of the stress-strain diagrams obtained above suggest that the oxymethylene chain may also be related to the β process, though the process is known to involve the motion of acyl chain. This point is discussed and confirmed later through the results of dynamic mechanical measurements.

Figures 2a and 2b respectively shows the variation of dynamic modulus E' and loss modulus E'' with temperature for CAcOM (A, B, C, and D). In the figures, the result for cellulose acetate is also included as a special case of CAcOM wherein the value of s is zero. With respect to E'' , three relaxation processes were observed for both cellulose acetate and four kinds of CAcOM within the experimental frequency and temperature ranges. They are labelled α_a , β_a and β'_a for cellulose acetate, and α , β and γ for four kinds of CAcOM, respectively, in order of decreasing tem-

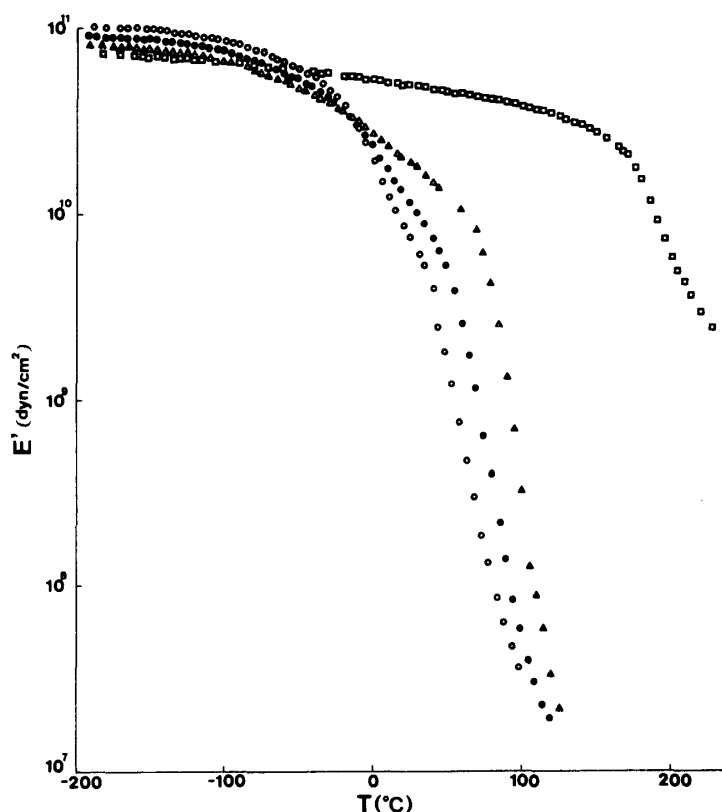


Fig. 2a. Temperature dependence of dynamic modulus E' for CAcOM (A, B, C, and D) and cellulose acetate. CAcOM (A): \triangle , (B): \bullet , (C) and (D): \circ Cellulose acetate: \square .

perature at which they were detected.

For cellulose acetate, the α_a and β_b processes have been reported respectively due to the micro-Brownian motion of the segment along the main chain and the motion including the acetate group in the side chain⁴⁾. In addition, in our previous study⁵⁾, the apparent activation energy ΔE for the α_a process was estimated to be more than 50 kcal/mol, while that for the β_a process to be less than 8 kcal/mol. Although these two processes were also observed by using dielectric measurements⁶⁾ in the corresponding frequency and temperature regions, the β'_a process could not be detected within the range examined. The β'_a process may be due to the local side chain motion around C-5 and C-6 axis of a glucopyranose ring. The α_a process will be discussed in the later paragraph in relation to the α process.

On the other hand, CAcOM from A to D exhibits quite different relaxation processes from those for cellulose acetate. Concerning the γ process in the Figure 2b, the maximum E'' values seems to increase as s increases, even if the influence of the β process is subtracted in E'' -temperature curves. The same results are also observed in this region for the other homologues of COA's as exemplified for (cellulose

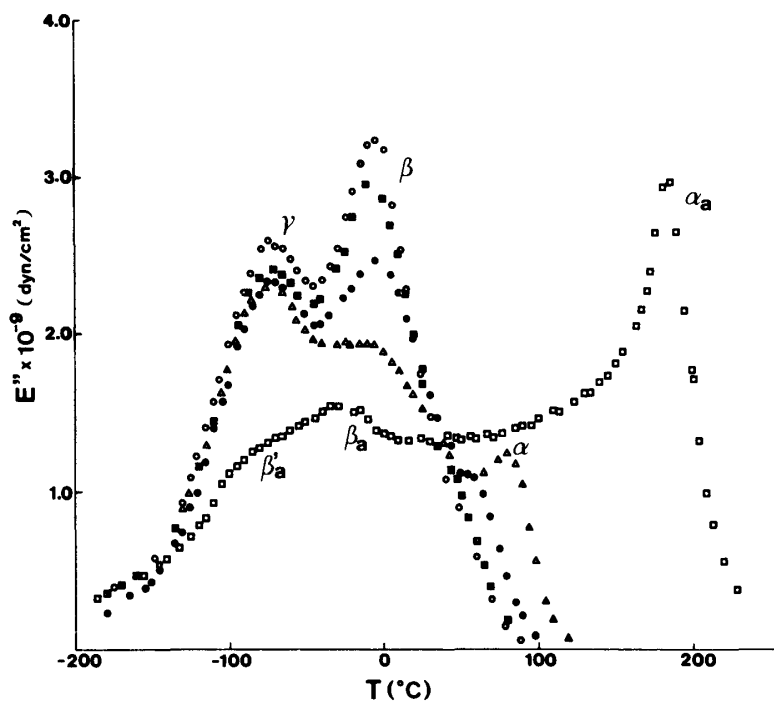


Fig. 2b. Temperature dependence of loss modulus E'' for CAcOM (A, B, C, and D) and cellulose acetate. CAcOM (A): \triangle , (B): \bullet , (C): \blacksquare , (D): \circ cellulose acetate: \square .

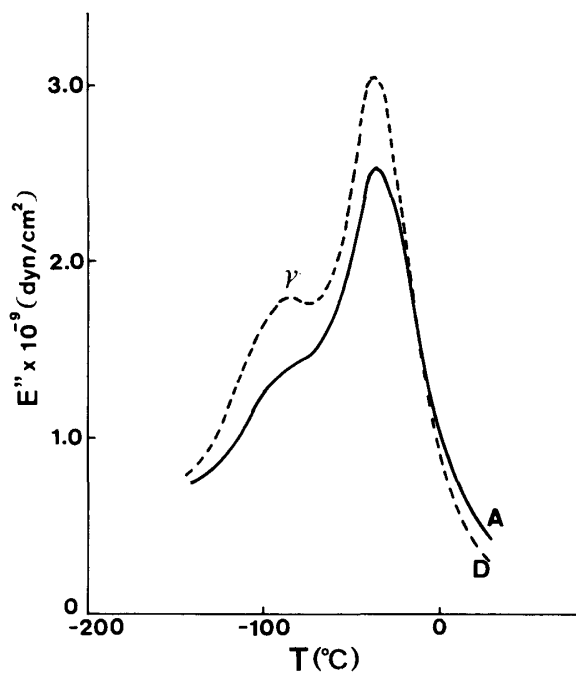


Fig. 3. Temperature dependence of loss modulus E'' for CVaOM (A and D).

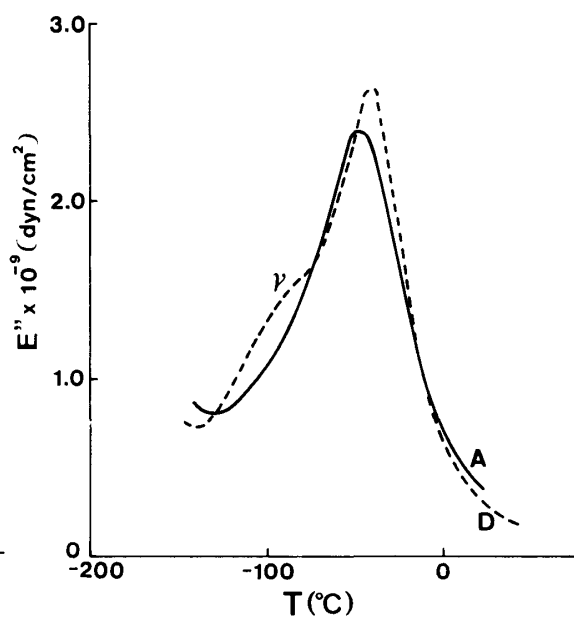


Fig. 4. Temperature dependence of loss modulus E'' for CHeOM (A and D).

oligo-oxymethylene ether) valerate, CV_aOM and hexanoate CH_6OM in Figures 3 and 4, respectively. This process has been considered to be the motion of the oxymethylene group in the side chain from the results of the dielectric measurements. If this is the case, the γ peak should increase in height as s increases, because in general the increase in the number of the motional unit responsible for the noted relaxation process causes increased peak height for polymers in the glassy state. Accordingly, from the results shown in figures 2, 3, and 4 the γ process is confirmed to be due to the motion of the oligo-oxymethylene group in the side chain.

The β process has been assigned to be due to the motion involving acyl side chain³⁾, since the process was largely affected by n . As shown in Figures 2a and 2b, however, both the maximum E'' values and the relaxation magnitude in the β region increase markedly also with increasing s . Hence, the β process is considered to include not only the motion of the acyl parts but also that of the oligo-oxymethylene parts in the side chain. For further information on the β process, note the E' -temperature curves for COA's. Figure 5 illustrates the variation of E' with temperature in the glassy state for a series of COA(D) from $n=2$ to 10. If comparisons

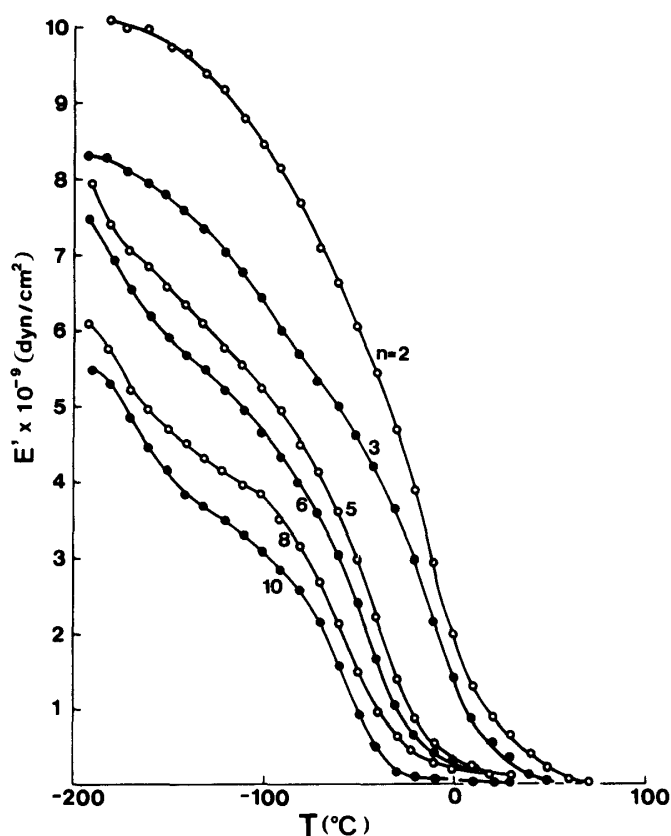


Fig. 5. Temperature dependence of dynamic modulus E' for a series of COA (D) from $n=2$ to 10.

are made at the same temperature, E' values decrease as n increases in the whole temperature range examined. The reason for this lowering was explained as follows: the increase in molecular size of non-polar n -alkyl group causes decreased interaction of polar ester group which arises from further separation of each main chain. It is of interest to note, however, that the trend in E' for COA in the glassy state when s increased is quite different from that when n increased. As shown in Figure 2a, E' -temperature curves for CAcOM along with cellulose acetate intersect at the temperature in the neighbourhood of the β region: with increasing s , E' values in the temperature range below the intersecting point increase, while they decrease above the point. The same results were also observed for other homologues of COA's when s increased. The reason for a rise in E' with s in the region below the β peak temperature can be ascribed to the increased interchain cohesive force resulting from the increased contents of polar oxymethylene groups. On the other hand, because changing length of the acyl or oxymethylene chains gives similar effect on the E' above the β region, the molecular motion of the oxymethylene chain is considered to be released enough to randomize their dipole orientation within the time scale observed, causing decreased interchain cohesive force. From these findings and discussion, the β process is concluded to be due to the segmental motion along the side chain which includes both the oxymethylene and acyl chains, i.e., $-(\text{CH}_2\text{O})_s\text{-COR}$.

However, regarding the β and γ processes, it is not yet clear that the motion of the side chain attached to which position of the three in the glucopyranose ring (i.e., C-6 and C-2 or C-3 positions) is responsible for these processes, though $-(\text{CH}_2\text{O})_s\text{-COR}$ side group is known to be introduced in these three positions. It is worth to remember that cellulose itself in the glassy state is known to exhibit a relaxation of OH side group attached to C-6 position. In this relation, it is most probable that the β and γ processes are stemmed from the internal motion of the side chain attached to C-6 position. Therefore, it is important to elucidate whether or not the motion within the side chain attached to C-2 and C-3 positions is responsible for the β and γ processes of COA. For this purpose, we investigated dynamic mechanical properties of xylan oligo-oxymethylene ether acylates which lack C-6 side chain. The variation of E' with temperature for xylan oligo-oxymethylene ether acetate, XAcOM and Hexanoate, XHeOH are respectively shown in Figures 6 and 7, in which the results for the corresponding COA's are also plotted. From the Figures, it is recognized that each xylan oligo-oxymethylene ether acylate exhibits two well-defined relaxation processes in the glassy state. The process in the lower temperature for XAcOM exhibits a marked peak while that for XHeOM appears as a shoulder. It can be seen that these processes agree well with the γ process of

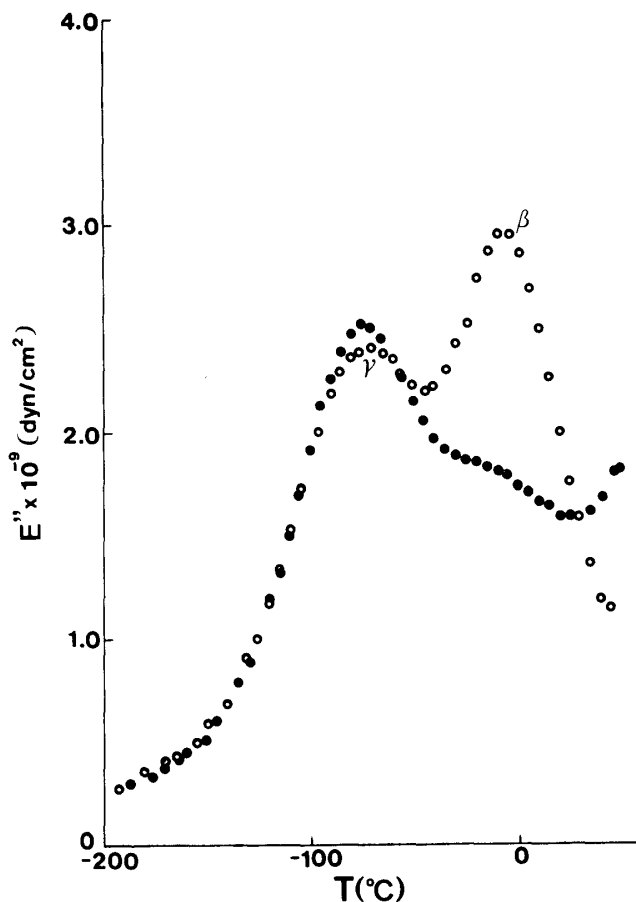


Fig. 6. Temperature dependence of loss modulus E'' for XAcOM (D), ● and CAcOM (D), ○.

the corresponding COA in both the magnitude and temperature location. On the other hand, the process in the higher temperature for XAcOM appears as a shoulder while that for XHeOM exhibits a peak. The location of the process corresponds closely to that of the β process for the corresponding COA. Furthermore, the trend in magnitude for E'' maxima in lower and higher processes of (xylan oligo-oxymethylene ether) acylates by changing side chain length is similar to that in the β and γ processes for COA³⁾. From these findings, the two processes (i.e., higher and lower processes) appearing in both XAcOM and CHeOM is concluded to be due to the motion of the oligo-oxymethylene parts in the side chain, and the micro-Brownian motion along the side chain, respectively. Therefore, the β and γ processes for COA are considered to stem from molecular motion of the side chain including not only at C-6 position but also at C-2 and C-3 positions. In this connection, it should be noted that the xylan derivatives prepared here are their first products applicable for film use.

In addition to the processes discussed above, the α process for COA and

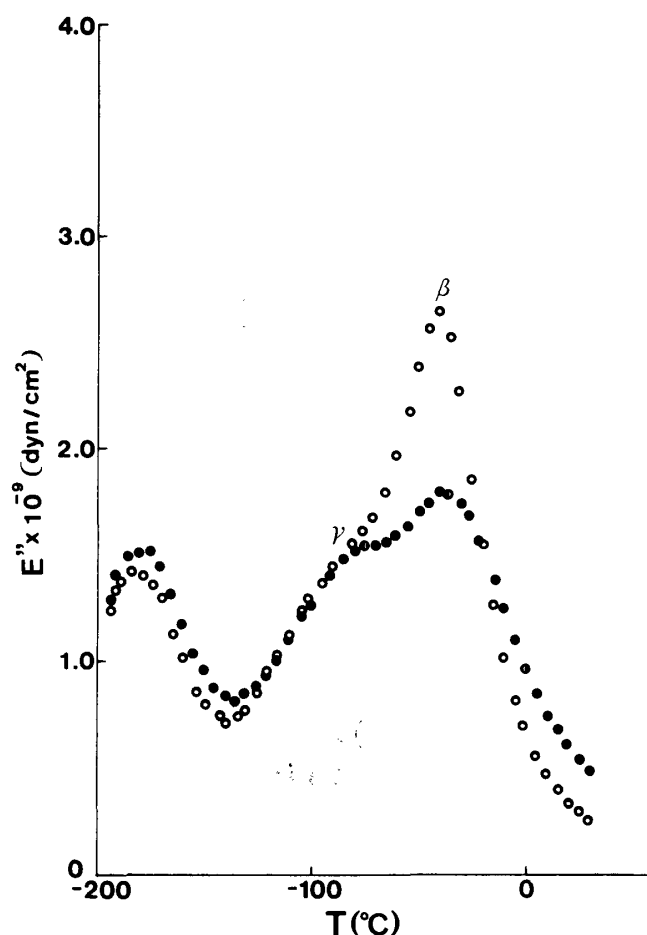


Fig. 7. Temperature dependence of loss modulus E'' for XHeOM (C), ● and CHeOM (D), ○.

α_a process for cellulose acylate are observed in higher temperature range as shown in Figure 2b for CAcOM and cellulose acetate. These processes have been regarded as due to the micor-Brownian motion of the main chain, and thus a considerable drop in E' in the corresponding region in Figure 2b is related to the glass rubber transition of the polymer. Therefore, the temperature location of E'' maximum in the α and α_a regions measured at such a low frequency as 110 Hz can be regarded as a rough measure of the glass transition point T_g of the samples. For cellulose acetate, T_g thus defined is located at about 180°C , while for CAcOM they appear considerably lower temperatures below 100°C . Furthermore, it can be seen that T_g of CAcOM moves to lower temperatures with increasing s . The similar results were also recognized for other COA's. Remind here that the lowering of T_g was also observed for COA when n increased³³. Because the polar oxymethylene group introduced in COA play a similar role to that of non-polar alkyl group on the β process, its influence to the subsequent α process must be similar. Therefore, the

reason for a lowering of T_g with increasing s from 0 to 2.2, can be interpreted in the same manner as the lowering of T_g with n : the introduction of the oxymethylene groups induces increased separation of each main chain, and additional introduction of the oxymethylene groups facilitate further separation of each main chain, resulting in a weakening of interchain cohesive force which causes a lowering of T_g .

As was seen above, each process for COA is largely affected by the change in length of the oxymethylene chain in the side chain in the same manner as that induced by the change in n , when the length of the acyl chain is short as in CAcOM. However, if the length of the acyl chain in COA is long enough as compared to that of the oxymethylene chain, the effect of the variation of s on each process may become small, because in such a case the ratio of the length of the oxymethylene chain to that of the side chain is small. Therefore, it is of interest to note whether or not the relaxation processes for COA having large n are affected by the variation of s . For elucidating this point, we note the influence of the oxymethylene chain length to the temperature location of the α process, i.e., T_g for COA.

Figure 8 shows the diagrams of T_g values determined from $\tan \delta$ maximum versus n for a series of COA (A, and D) and cellulose acylates. In the Figure, the results for a series of polyalkylmethacrylates is also quoted for reference. At $n=2$,

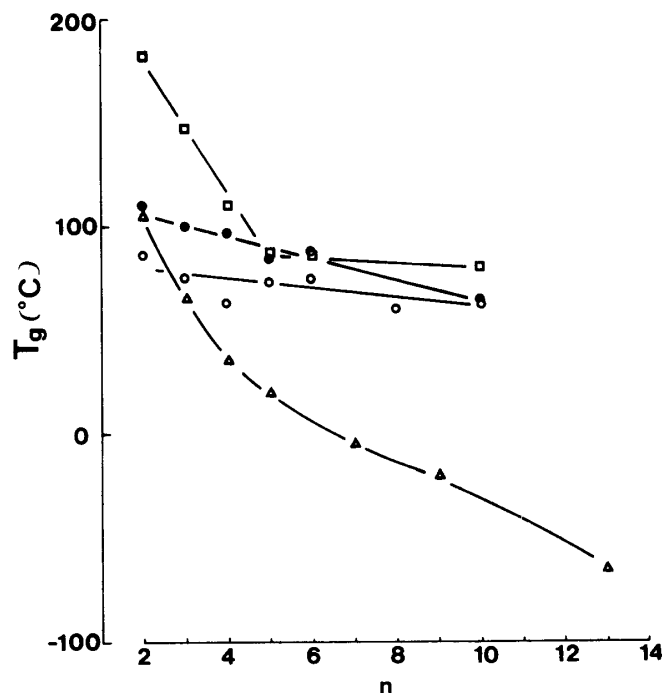


Fig. 8. Relationship between T_g and n for a series of COA (A and D), cellulose acylates and polyalkylmethacrylates. CAcOM (A): ●, CAcOM (D): ○, cellulose acylates: □, polyalkylmethacrylates: △.

the difference in T_g with s among COA (A), (D), and cellulose acylate is very large, while it decreases markedly as n increases, and finally little difference in T_g is observed at $n=10$. Consequently, it is known that T_g of COA with large n do not vary in a great extent with the length of the oxymethylene chain within the range examined. In this connection, it should be noted that T_g reduction for both COA's and cellulose acylates levels off above room temperature. On the other hand, cellulose derivatives having linear and flexible side chain are known to exhibit lower T_g values than those of cellulose derivatives with bulkier side chain, when their molecular weight is the same in the side chain portion⁷⁾. Therefore, based on the results that even the cellulose derivatives with linear and flexible side chain exhibit a lower limit of T_g above room temperature, it is suggested that all the cellulose

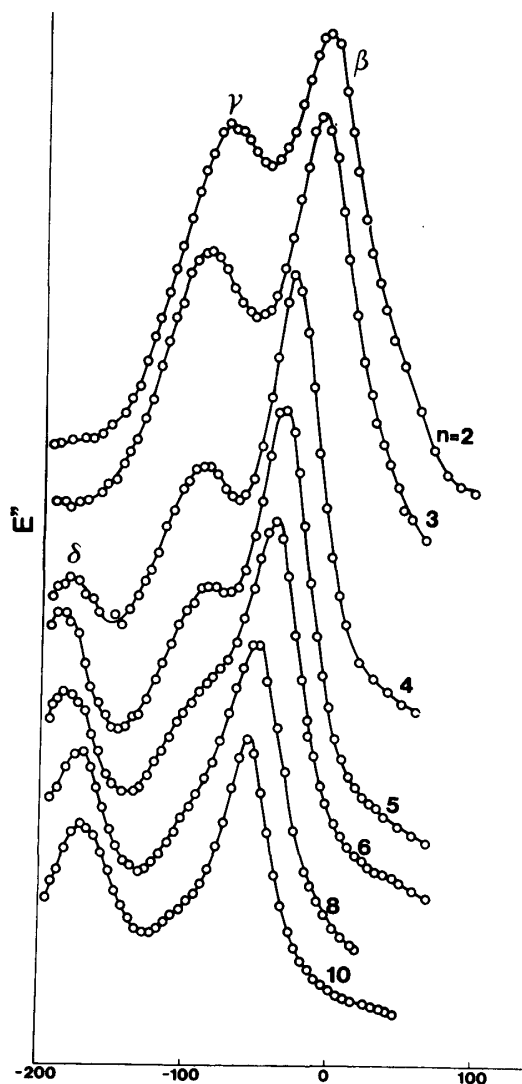


Fig. 9. Temperature dependence of loss modulus E'' for a series of COA (D) from $n=2$ to 10.

derivatives have a lower limit of T_g above room temperature. In contrast, the lowering of T_g for polyalkylmethacrylates proceeds quite different manner from that for COA as shown in the Figure. In this series, T_g decreases with increasing n , showing no levelling off. The difference between cellulose derivatives examined here and poly- n -alkyl methacrylates, both having linear and flexible side chain, may be attributed to the different structure of the main chain: the former is bulkier than the latter.

The extent of the contribution of the oxymethylene chain to the relaxation processes for COA is more directly reflected to the β and γ processes in the glassy state because they are related to the motion involving oxymethylene chain itself. Figure 9 illustrates the plots of E'' with linear, arbitrary scale against temperature for a series of COA(D) from $n=2$ to 10 in the temperature range from -190°C to 100°C . It can be seen that even if n increases the γ region which results from the oxymethy-

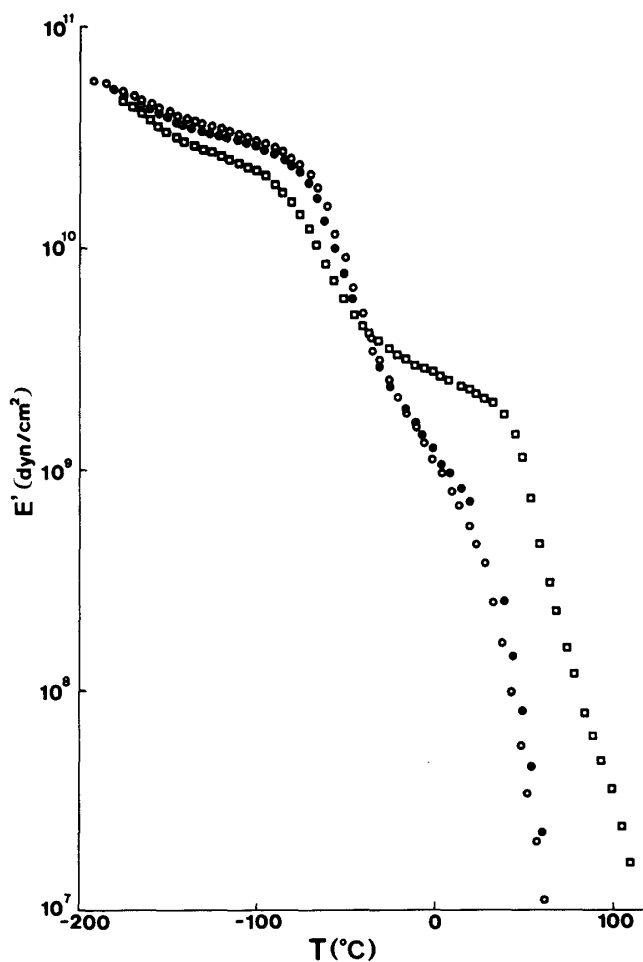


Fig. 10a. Temperature dependence of dynamic modulus E' for CDeOM (A, D) and cellulose decanoate. CDeOM (A): ●, (D): ○ cellulose decanoate: □.

lene portion remains at a constant temperature of about -70°C , though the neighbouring β region shifts to lower temperature. Furthermore, the γ peak which is clearly visible for COA with $n=2$ become less distinct, and finally for COA with $n=10$, i.e., (cellulose oligo-oxymethylene ether) decanoate, CDeOM, it merged completely in the low temperature tail of the β peak. On the other hand, the additional δ process is seen to appear below -160°C for COA above $n=4$. However this process is not related to the molecular motion in the oxymethylene portion, since it is considered to be the motion of three or more methylene groups in a row in the side chain, which occurs in the freezed state of the molecular motion in the oxymethylene portion. From these results, viscoelastic properties of COA with large n is expected to be little affected by the values of s .

Figures 10a and 10b show the variation of E' and E'' , respectively, for CDeOM (A, D) and cellulose decanoate whose n values are the largest in the series examined. As is expected, all the relaxation processes appearing in both CDeOM (A) and CDeOM (D) seem similar despite their different s values. Furthermore, it should be noted that this similarity is also recognized in the relaxation processes for CDeOM (A, D) and cellulose decanoate which lacks the oxymethylene proton in the side chain. From this result, it is concluded that the role of the oxymethylene group to the relaxation mechanism of COA becomes negligibly small when n is large.

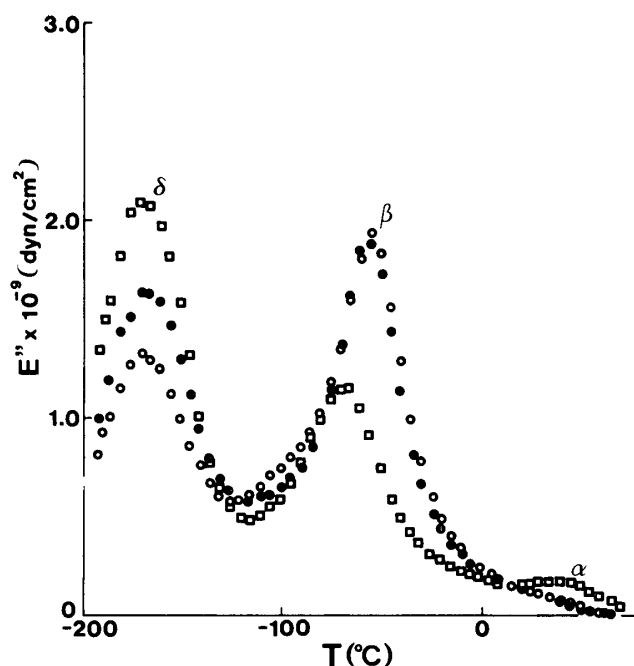


Fig. 10b. Temperature dependence of loss modulus E'' for (A, D) and cellulose decanoate.

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